A review of *in situ* measurement of organic compound transformation in groundwater†‡

Sharon K Papiernik*
USDA—Agricultural Research Service, George E Brown Jr Salinity Laboratory, 450W Big Springs Road, Riverside, CA 92507-4617, USA

Abstract: Laboratory assessments of the rate of degradation of organic compounds in groundwater have been criticized for producing unrepresentative results. The potential for organic compounds to be transformed in groundwater has been measured using *in situ* methods, which avoid problems of attempting to duplicate aquifer conditions in the laboratory. *In situ* assessments of transformation rates have been accomplished using transport studies and *in situ* microcosms (ISMs); a review of these methods is given here. In transport studies, organic solutes are injected into an aquifer and the concentrations are monitored as they are transported downgradient. The change in mass of a solute is determined by the area contained under the breakthrough curve (plot of concentration versus time). ISMs isolate a portion of the aquifer from advective flow and act as *in situ* batch reactors. Experiments using ISMs involve removing water from the ISM, amending it with the solutes of interest, re-injecting the amended water, and monitoring the solute concentrations with time. In both transport and ISM studies, the loss of organic solutes from solution does not allow a distinction to be made between sorptive, abiotic and biotic transformation losses. Biological activity can be chemically suppressed in ISMs and the results from those experiments used to indicate sorption and abiotic loss. Transformation products may be monitored to provide additional information on transformation mechanisms and rates.
Published in 2001 for SCI by John Wiley & Sons, Ltd

Keywords: transformation; degradation; groundwater; organic

1 INTRODUCTION

The complex nature of sub-surface environments complicates assessments of the potential for degradation of organic compounds. Dynamic conditions of microbial population, pH, Eh, concentration of nutrients and other solutes exist in the subsurface. Many of these parameters are difficult to control in the laboratory, prohibiting duplication of aquifer conditions. Recently, *in situ* methods have been promoted as an improvement over laboratory procedures for measuring degradation. Experiments conducted *in situ* are advantageous because they may be conducted with minimal disturbance of the natural aquifer conditions. *In situ* methods indicate the overall dissipation potential of an organic compound in groundwater under certain conditions, although in most circumstances they may not provide information on the mechanism of dissipation. Because multiple processes act concurrently, including sorption/desorption and chemical and biological degradation, interpretation of results of *in situ* experiments may be difficult.

In situ methods to measure transformation of organics in groundwater may be grouped into two general categories: those using flowing systems (transport studies) and those using static systems (*in situ* microcosms). This review discusses the methods used to conduct and interpret experiments using both these *in situ* approaches and also the results of studies of the degradation rate of organic compounds in groundwater.

2 *IN SITU* TRANSPORT STUDIES

In transport studies, the concentration and distribution of solutes are monitored in groundwater to derive transport parameters, including transformation rates. Transport studies may be conducted under a natural gradient, where the flow field remains relatively unaltered, or under a forced gradient, where the groundwater flow rate is increased by pumping from an extraction well.

2.1 Instrumentation

In transport experiments, solutes are injected into the

* Correspondence to: Sharon K Papiernik, USDA—Agricultural Research Service, George E Brown Jr Salinity Laboratory, 450W Big Springs Road, Riverside, CA 92507-4617, USA
E-mail: spapiernik@ussl.ars.usda.gov
† Based on a paper given at the symposium 'Degradation of Pesticides in Subsoil and Groundwater' organised by Dr Margaret Mills on behalf of Zeneca Agrochemicals, Monsanto and Aventis CropScience and held at the Third SETAC World Congress held at Brighton, UK, 21–25 May, 2000

(*Received 20 May 2000; revised version received 20 September 2000; accepted 16 October 2000*)

zone of interest and their concentration and three-dimensional distribution are monitored as they are transported downgradient. Alternatively, an existing solute plume may be monitored to determine transport and degradation parameters. The three-dimensional delineation of the solute plume is accomplished through a series of multi-level samplers, which are installed downgradient from the injection well(s) with the central axis of the samplers located along the direction of groundwater flow. A general instrumentation scheme for natural and forced gradient transport studies in shallow sand and gravel aquifers is shown in Fig 1. Multi-level samplers are typically constructed of polymeric and/or stainless steel materials, and include ports for sampling at multiple depths at each latitude/longitude location (Fig 1c). Multi-level samplers act as bundled miniature wells: tubing connected to each sampling port extends to the surface.

Materials must be chosen to be compatible with the solutes of interest and also with the existing groundwater chemistry. Sorption of organics to polymeric materials has been reported;[1–5] many of these studies indicate that flexible polymeric materials are more sorptive than rigid polymers. Metals used in groundwater samplers can transform (dehalogenate) polyhalogenated organic compounds.[2] Therefore the purging of stagnant water and the flow rate used during sampling must be sufficient to achieve representative samples. Constant analyte concentrations have been observed after purging three casing volumes from sampling wells.[6] When the solutes sorb significantly to the tubing material, a relatively high flow rate (such as 1 liter min^{-1}) may be required to minimize sorptive losses during sampling.[7] Where sampling points are very dense, the purging and flow rate used must not interfere with the collection of discrete samples representative of the immediate area surrounding each sampling point.

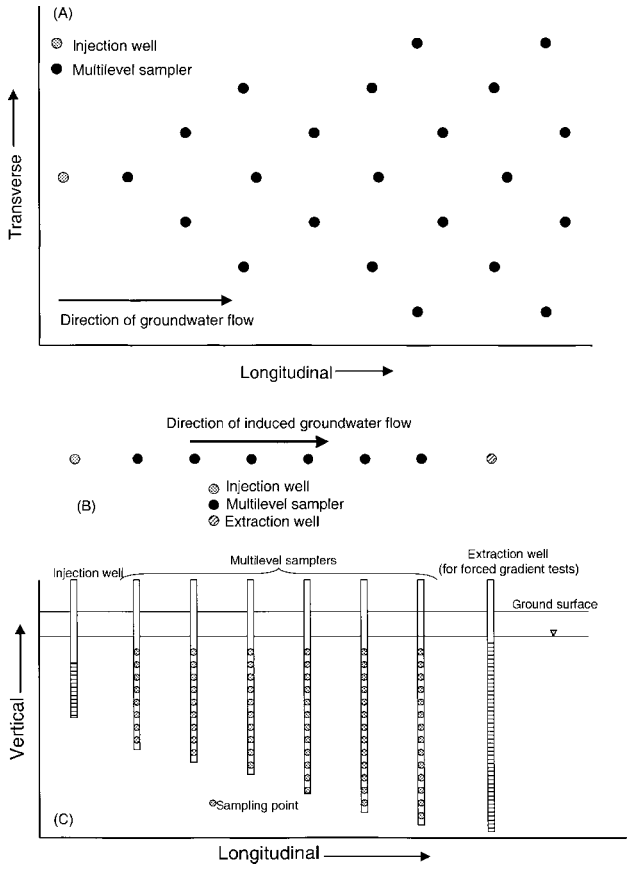

Figure 1. General scheme of field instrumentation for transport studies conducted under (A) a natural gradient[18] and (B) forced gradient. (C) Depth cross-section is similar for both approaches.

Other potential sources of sampling bias include losses due to volatilization, sorption to the sample container and degradation prior to analysis. Water samples containing volatile solutes must be collected in a way that eliminates losses to the vapor phase. Minimizing exposure to the atmosphere and including no headspace in sample containers reduces volatile loss. Samples should be stored at low temperatures and analyzed soon after collection to reduce degradative losses prior to analysis.

2.2 General procedure for transport studies

The injection solution is prepared in water from the site. The solutes of interest are included at the desired concentration and a conservative tracer (such as sodium bromide or tritiated water) is included to indicate the behavior of a non-sorbed, non-degraded compound. The injection solution (several hundred liters) is pumped into the injection well(s) at a constant, slow rate so as to minimize disturbance of the flow field. During injection, the water near the injection well is displaced by the injected solution, resulting in little dilution. Samples are collected from the downgradient multi-level samplers to provide 'snapshots' of the solute distribution at each sampling time (Fig 2). The concentration at each sampling point may be plotted as a function of time to produce a breakthrough curve for each solute (Fig 3). Solute concentrations are usually normalized to the injected concentration (C_0), producing a relative concentration.

2.3 Determining persistence in transport studies

The extent of degradation in transport studies is usually determined by calculating the mass remaining in the system or by fitting the data to the advection–dispersion equation, which includes a degradation term.

2.3.1 Calculation of mass remaining

The mass of conservative tracer is essentially constant throughout the experiment, since sampling removes only a small proportion of the injected mass. An estimate of the mass of each solute may be determined by integrating the mass in each volume element

$$\text{mass} = nCzA \qquad (1)$$

over the total number of sampling points.[8] In this case, the volume associated with each sampling point is

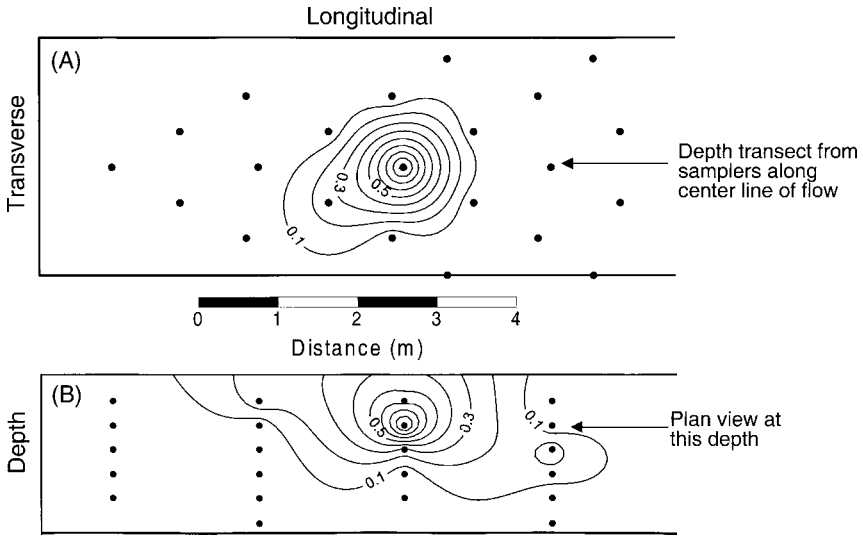

Figure 2. Contour plots for conservative tracer (bromide) one month after injection in natural gradient study conducted by Widmer and Spalding.[18] (A) plan view, (B) depth cross-section.

given by the triangular horizontal area element (A) and vertical depth z which is the sum of one-half the distance to the sampling points directly above and below it. C is the concentration at the sampling point representing the volume element and n is porosity. The total mass is the sum of the mass contained in each volume element. For conservative solutes, the mass remains unchanged from the mass at early times or the injected mass. The use of this approach to determine mass is affected by the sampling density, because portions of the solute plume may be outside the sampling points.[9] This approach may underestimate the actual total mass present.[10] The remaining mass as a function of time after injection provides an estimate of the transformation rate, but the trend should not be used to infer reaction order.[10]

2.3.2 *Area under breakthrough curves*

The mass of each solute may also be normalized to the mass of tracer to provide an indication of total mass loss during the experiment. The area under the breakthrough curve provides a measure of mass. The area may be calculated by the zeroth moment

$$\text{Area} = \sum_{i=1}^{n} C_i \Delta t \tag{2}$$

where C_i is the relative concentration, t is time, and n is the number of samples defining the breakthrough curve. Alternatively, the area may be measured by fitting a non-linear curve to the data and determining the peak area.[11] An indication of the degradation occurring during the experiment is given by comparing the solute areas, normalized to the conservative tracer. For persistent solutes, the relative area remains approximately one throughout the experiment. Solutes that show appreciable decreases in relative area are undergoing some mass loss process, either by transformation or irreversible sorption/slow desorption.

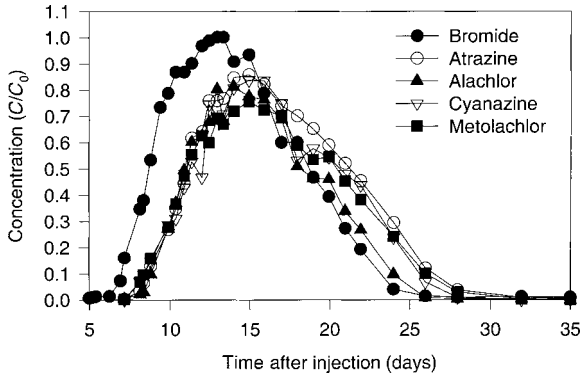

Figure 3. Breakthrough curves for one sampling point in natural gradient study conducted by Widmer and Spalding.[18]

2.3.3 *Non-linear regression to advection–dispersion equation*

Another approach to determining the rate of degradation in transport experiments is to fit the breakthrough curves to the advection–dispersion equation with first-order decay:[12]

$$A(x,t) = \frac{C_0}{2}\left[\exp\left(\frac{vx(1-m)}{2D}\right)\ \text{erfc}\left(\frac{Rx - mvt}{\sqrt{4DRt}}\right) + \exp\left(\frac{vx(1+m)}{2D}\right)\ \text{erfc}\left(\frac{Rx + mvt}{\sqrt{4DRt}}\right)\right] \tag{3}$$

$$C = A(x,t) \text{ for } t \le t_0$$

$$C = A(x,t) - A(x, t - t_0) \text{ for } t > t_0$$

where

$$m = \sqrt{1 + \frac{4kD}{v^2}}$$

C is the solute concentration, C_0 is the mean injected concentration, v is the groundwater transport velocity,

x is the distance from the injection well to the sampling point, D is the hydrodynamic dispersion coefficient, R is the retardation factor ($v_{groundwater}/v_{solute}$), t_0 is the pulse width (time) and k is the first-order degradation constant. Non-linear regression of tracer C versus t data gives values for v, D and t_0 at each sampling point. Non-linear regression of solute data gives estimates of R and k for each solute by fixing x at its appropriate value, and using the regression values for tracer data (v, D, and t_0) at the same sampling point. Use of this approach for experimental data from a transport study indicated that it predicted greater loss than that determined by the decrease in peak area.[11]

Transport studies using injections of solutes into groundwater have been used to measure the retention and degradation of halogenated hydrocarbons,[8,13,14] aromatic hydrocarbons[8,10,15] and pesticides.[16–18] A summary of the results of these experiments is given in Table 1.

3 *IN SITU* MICROCOSMS

Transport studies are expensive and groundwater flow is complex, affected by aquifer heterogeneity and temporal and spatial variability in groundwater flow. Therefore, changes in concentration are difficult to ascribe to a given process, and transport studies may not be good indicators of solute persistence. *In situ* microcosms (ISMs) are gaining in popularity to determine the degradation potential of organic compounds in groundwater. ISMs isolate a portion of the aquifer from advective flow, so the only processes affecting solute concentrations are dilution, sorption/desorption and transformation. ISMs have been used for determining the rate of degradation of hydrocarbons,[15,19–23] substituted aromatics,[20,24] halogenated hydrocarbons[15,20–23] and herbicide compounds[16,25] in groundwater (Table 2).

3.1 Instrumentation

In situ microcosms are installed below the water table. They follow the general design of Gillham *et al*,[19] in which a point sampler is installed in a test chamber which is open at the bottom to allow exchange with the aquifer (Fig 4). A main screen is used for the injection or withdrawal of large volumes of water, and a small, screened sampler in the test chamber is used to collect water samples throughout the experiment to monitor solute concentrations. ISMs of this general design have been modified in size and sampling apparatus.

Table 1. Degradation determined in *in situ* transport studies

Compound	*Observed mass loss*
Aromatic hydrocarbons	
Benzene	75% in 108 days;[10] 97% in 440 days;[8] NS[a] in 50 days[b,15]
Toluene	95% in 81 days;[10] 100% in 50 days[b,15]
o-Xylene	75% in 53 days;[10] NS in 50 days[b,15]
m-Xylene	67% in 28 days;[10] mass loss not determined, but transformation indicated in 50 days[b,15]
p-Xylene	80% in 28 days;[10] 99% in 440 days[8]
Ethylbenzene	NS in 50 days[b,15]
1,2,4-Trimethylbenzene	NS in 50 days[b,15]
Naphthalene	96% in 440 days[8]
Halogenated hydrocarbons	
Bromoform	>80% in 700 days[13]
Carbon tetrachloride	NS in 700 days,[13] <10 days[b,14]
Tetrachloroethene	NS in 700 days,[13] <10 days[b,14]
Hexachloroethane	>80% in 700 days[13]
Dichlorobenzene	>80% in 700 days;[13] 93% in 440 days[8]
Herbicide compounds	
Atrazine	NS in 100 days,[18] 160 days,[16] >5 days[b,17]
Cyanazine	NS in 60 days,[18] >5 days[b,17]
Simazine	~35% in >5 days[b,17]
De-ethylatrazine	NS in 100 days[8]
De-isopropylatrazine	NS in 100 days[8]
MCPP	Mass loss not determined, but transformation indicated in 160 days[16]
Alachlor	~40% in 60 days;[18] ~30% in >5 days[b,17]
Butachlor	~70% in 60 days[18]
Metolachlor	NS in 60 days:[18] ~20% in >5 days[b,17]
Propachlor	~20% in >5 days[b,17]
Detergents	
Alkyl benzene sulfonate	NS[c,32]
Linear alkyl sulfonate	Mass loss not determined, but transformation indicated[c,32]
Sodium dodecyl sulfate	Mass loss not determined, but transformation indicated[c,32]

[a] No significant mass loss during the experiment.

[b] Forced gradient test, results based on two sampling points.

[c] Monitoring of an existing plume.

Table 2. Degradation measured using *in situ* microcosms, based on decrease in concentration with time

	Observed mass loss under specific redox conditions			
Compound	*Methanogenic*	*Iron-reducing*	*Denitrifying*	*Aerobic*
Aromatic hydrocarbons				
Benzene	NS[a] in 100 days,[15] 150 days,[20] 180 days[23]	NS in 120 days,[20] 200 days[23]	NS in ~30 days,[19] 80 days[20]	40% in 10 days[19] ~100% in 20 days[21,22]
Toluene	NS in 150 days,[20] 180 days[23] 99% in 20 days[15]	NS in 120 days[20] 100% in 200 days[b,23]	NS in 80 days[20]	100% in 20 days[22]
o-Xylene	NS in 80 days,[15] 150 days,[20] 180 days[23]	NS in 120 days,[20] 200 days[23]	NS in 80 days[20]	100% in 100 days[21,22]
m/p-Xylene	NS in 180 days[23] 100% in 20 days,[15] 50 days[b,15]	NS in 180 days[23]		
Ethylbenzene	NS in 180 days[23] 50% in 100 days[15] 100% in 30 days[15]	NS in 200 days[23]		
1,2,4 Trimethylbenzene	100% in 100 days[b,15]			
Cumene	NS in 100 days[15] 100% in 80 days[15]			
Biphenyl	NS in 150 days[20]	NS in 120 days[20]	NS in 80 days[20]	100% in 100 days[22]
Naphthalene	NS in 80 days,[15] 150 days,[20] 180 days[23]	NS in 120 days,[20] 180 days[23]	NS in 80 days[20]	100% in 20 days[22]
Nitrobenzene		>80% in 60 days[20]	>80% in 60 days[20]	
Halogenated hydrocarbons				
Carbon tetrachloride	>80% in 60 days[20] 100% in 20 days[23]	>80% in 60 days[20] 100% in 20 days[23]	NS in 80 days[20]	NS in 100 days[22]
1,1,1-Trichloroethane	>80% in 60 days[b,20] >90% in 200 days[23]	NS in 120 days[20] >80% in 200 days[23]	NS in 80 days[20]	NS in 50 days[22]
Trichloroethene	NS in 150 days[20] >90% in 200 days[b,23]	NS in 120 days[20], 200 days[23]	NS in 80 days[20]	NS in 70 days[22]
Tetrachloroethene	>90% in 200 days[b,23]	NS in 120 days,[20] 200 days[23]	NS in 80 days[20]	NS in 70 days[22]
Chlorobenzene	NS in 100 days[15]			
o-Dichlorobenzene	NS in 150 days[20]	NS in 120 days[20]	NS in 80 days[20]	~90% in 100 days[22]
p-Dichlorobenzene	NS in 150 days[20]	NS in 120 days[20]	NS in 80 days[20]	~80% in 100 days[21,22]
Phenolic compounds				
Phenol	NS in 150 days[24]	>80% in 60 days[b,24]	NS in 80 days[24]	100% in 20 days[22,26]
o-Cresol	NS in 150 days[24]	NS in 120 days[24]	NS in 80 days[24]	100% in 20 days[22]
o-Nitrophenol	>90% in 10 days[24]	>90% in 10 days[24]	>80% in 60 days[24]	~90% in 100 days[22]
p-Nitrophenol	>90% in 10 days[24]	>80% in 60 days[24]	<80% in 60 days[24]	100% in 20 days[22,26]
2,4-Dichlorophenol	<80% in 60 days[24]	NS in 120 days[24]	NS in 80 days[24]	100% in 100 days[22,26]
2,6-Dichlorophenol	>80% in 60 days[b,24]	NS in 120 days[24]	NS in 80 days[24]	~80% in 100 days[22,26]
4,6-*o*-Dichlorocresol	NS in 150 days[24]	NS in 120 days[24]	NS in 80 days[24]	
Herbicide compounds				
Atrazine			NS in 45 days[25]	NS in ~100 days[16]
De-ethylatrazine			NS in 45 days[25]	
De-isopropylatrazine			NS in 45 days[25]	
MCPP				NS in ~50 days[16]

[a] No significant mass loss during the experiment.
[b] Degradation observed following a lag phase.

They are generally constructed of stainless steel and typically enclose two liters or more of the aquifer.

Installation of ISMs below the water table has been accomplished through an augered borehole or, for very shallow aquifers, through an excavated hole. ISMs may be installed through a hollow-stem auger by drilling to the depth of installation, delivering the ISM to the bottom of the auger stem, and using a vibrating hammer to force the ISM into the aquifer. For a very shallow aquifer (depth ~3 m), ISMs have been installed by excavating to just above the water table, shoring the hole to provide access to the ISM, and

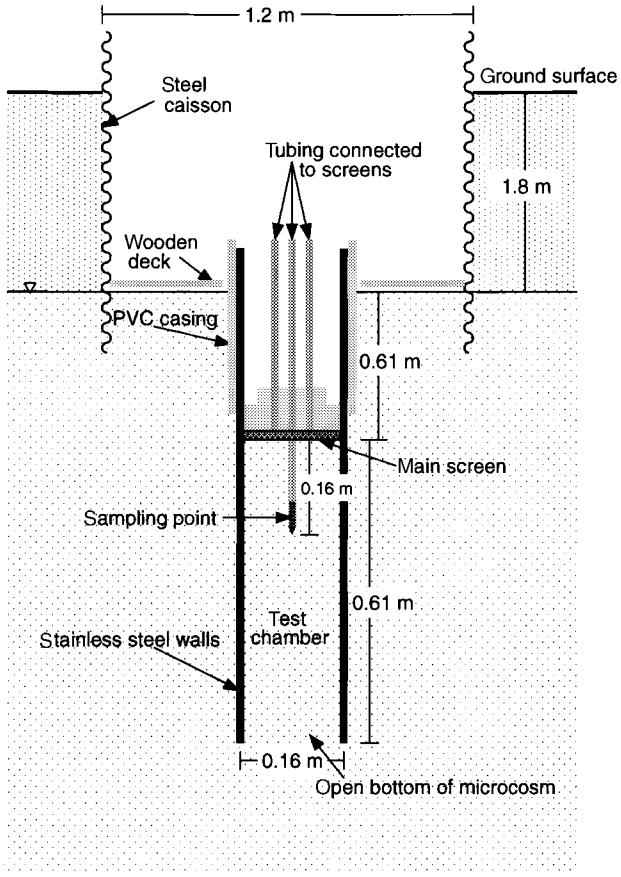

Figure 4. Schematic diagram of an *in situ* microcosm as described in Reference 25. Modifications of this general design are described in References 15, 19 and 26.

vibrating the ISM into the aquifer.[25] Several pore volumes of water are removed slowly following ISM installation to re-establish natural aquifer conditions.

While the installation of the ISM may slightly change the bulk density of the matrix, other parameters which are difficult to control in laboratory experiments, including pH, Eh, microbial population, and composition of the aquifer matrix and groundwater remain unaltered. Stagnant water is removed from the ISM before beginning an experiment. Water for the experiment is withdrawn from the ISM without exposure to the atmosphere, spiked with the compounds of interest, and re-injected into the ISM through the main screen. Samples are collected from the ISM test chamber using a syringe; tubing volume is small to minimize the volume required to flush and discard before sample collection. This is important because of the relatively small volume of water contained in most ISMs (<1 liter).

3.2 General procedure for ISM experiments

Water is removed from the ISM, and pumped through gas-impermeable tubing into an evacuated, sealed collection vessel. The solutes whose degradation are to be determined are added to the vessel, along with a non-sorbed, non-degrading tracer (bromide or tritiated water). Solutes to manipulate the redox conditions in the ISM may also be added, such as additional oxygen,[22] nitrate plus ethanol, which induced denitrifying conditions in an aerobic aquifer,[25] or growth substrates for anaerobic bacteria.[15] Sterilized controls may be included by poisoning the water with formaldehyde or sodium azide. The volume of water removed and re-injected is typically more than three pore volumes contained in the ISM to ensure that the water in the ISM is completely displaced by the amended water.

Samples are collected periodically for solute determination; sampling frequency is dependent on the rate of degradation of the compounds of interest. Additional samples may be analyzed for redox status and microbial activity.[26] As in all sampling procedures, the dead volume of the tubing must be flushed and sample collection, storage and analysis must not result in volatile or other losses.

3.3 Determining persistence in ISM studies

Because multiple processes are reducing solute concentrations, including dilution, sorption and degradation, the concentration data obtained in ISM experiments must be interpreted carefully.

3.3.1 Dilution

Normalizing reactive solute concentrations to those of the conservative tracer accounts for dilution in the ISM. Because the bottom of the ISM is open, withdrawing water from the ISMs for sample analysis results in unamended aquifer water being drawn into the ISM. Typically, very little dilution is observed for ISMs until they are impacted by dilution with unamended water. Dilution at early times could indicate a leaking ISM, hydraulic conditions in the ISM during loading that resulted in non-uniform concentrations throughout the ISM, or a change in density with addition of amendments causing a downward flux of amended water. Data from ISMs showing early dilution should not be analyzed using these methods to calculate *in situ* degradation rates.[26]

3.3.2 Sorption and degradation

If the organic solutes in the ISM indicate a decrease in concentration relative to the conservative tracer, there may be mass loss due to sorption and/or degradation. The interpretation of the results becomes similar to those obtained in a laboratory incubation, where solute concentrations may be impacted by sorption/desorption and transformation reactions. Because multiple processes are occurring simultaneously, and because there is usually no effective way to separate the processes, the calculation of transformation rates from ISM data depends on the impact of each process affecting the solute.

Microbial degradation can be minimized by poisoning the system with formaldehyde or sodium azide.[21,22] In this case, the biologically inhibited ISM serves to indicate the extent and kinetics of sorption and abiotic degradation. The additional concentration

decline observed in a biologically active ISM is interpreted as being due to biotic transformation. This method is useful only for determining biological degradation rates, since abiotic degradation, which occurs in both the biologically active and inactivated ISMs, would be subtracted out.

Sorption has also been determined in laboratory or field tests and the results applied to the concentration changes observed in an ISM to differentiate sorption from transformation. Laboratory batch-derived sorption parameters did not describe the initial decrease and shape of the concentration versus time curve in a biologically inhibited ISM.[21] Sorption/transport parameters have been obtained using ISMs in a manner analogous to laboratory miscible displacement experiments.[27,28]

Sorption of organic solutes to aquifer material may be very slow,[29] and may be concentration-dependent. A kinetic model of organic sorption is given by the two site/two region model.[30] Such models include terms indicating the fraction of sorptive sites that are at equilibrium, a partitioning coefficient (K_d), and a kinetic parameter that describes sorption to the non-equilibrium sites. The processes resulting in the kinetic sorption behavior described by the two site/two region model determine the physical/chemical interpretation of the model parameters. Bjerg *et al*[21] determined sorption parameters using laboratory batch reactors, then fitted the data from a biologically deactivated ISM to the two site/two region model (fixing K_d at the laboratory-derived value) to obtain values for the fraction of equilibrium sorption sites and the kinetic sorption parameter.

3.3.3 *Analysis of transformation products*

If the mechanism of degradation is known (eg dehalogenation), transformation products may be monitored to separate degradation from sorption processes. In the case of halogenated organic compounds, many processes result in dehalogenation, including hydrolysis, microbial dehalogenation and nucleophilic substitution, producing the halogen ion and dehalogenated organic compound(s). For a singly halogenated compound that degrades via dehalogenation, monitoring of the halogen ion may provide a useful measure of degradation. Isotopic labeling may be useful for identifying transformation products when the organic compound is mineralized. Alterations of the enantiomeric ratio of a chiral herbicide have been used as evidence of transformation *in situ*.[31] In general, unless the transformation products are non-sorbed and indicate mass conservation, monitoring transformation products provides evidence that degradation is occurring, but may not be useful for separating sorption and degradation processes quantitatively.

3.3.4 *Transport in ISMs*

ISMs isolate a portion of the aquifer from overall advective flow. During injection, there is a relatively high flow rate as the amended water is injected through the main screen of the ISM. During sampling, small volumes of water are removed at relatively low flow rates. For ISM experiments in which the total volume of water removed with sampling is small compared with the total volume of the ISM, it may be sufficient to assume that the ISM remains well-mixed at all times, resulting in no or only a small amount of dilution with sampling.

In most cases, a detailed assessment of the processes impacting solute concentrations is not warranted, but ISMs are useful for indicating the potential for solute transformation in groundwater and a general indication of reaction rates (hours, days, months or years). They have also been used rather extensively to examine the relative reactivity of solutes under different redox conditions (Table 2).

4 CONCLUSIONS

In situ experiments are a valuable means of determining the potential for degradation of organic compounds in groundwater. Studies which included a transport study and ISMs installed at the same site have indicated that these approaches produce generally consistent results in terms of the degradability of organic compounds.[15,16] Experiments which have compared *in situ* studies and laboratory batch reactors under similar environmental conditions have indicated that many compounds demonstrate a lower susceptibility to degradation in laboratory microcosms than in transport studies[15,16] and ISMs;[15,20,22,24] however, for some compounds, results from laboratory and *in situ* microcosms generally agree.[16,20,22,24] Additional research is needed to assess the ability of these *in situ* methods to predict the long-term behavior of organic compounds in groundwater.

REFERENCES

1 Barcelona MJ, Helfrich JA and Garske EE, Sampling tubing effects on groundwater samples. *Anal Chem* **57**:460–464 (1985).
2 Reynolds GW, Hoff JT and Gillham RW, Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ Sci Technol* **24**:135–142 (1990).
3 Topp E and Smith W, Sorption of the herbicides atrazine and metolachlor to selected plastics and silicone rubber. *J Environ Qual* **21**:316–317 (1992).
4 Parker LV and Ranney TA, Sampling trace-level organic solutes with polymeric tubing. Part I. Static studies. *Ground Water Monit Remed* **17**:115–124 (1997).
5 Ranney TA and Parker LV, Comparison of fiberglass and other polymeric well casings. Part II. Sorption and leaching of trace-level organics. *Ground Water Monit Remed* **18**:107–112 (1998).
6 Papiernik TD, Widmer SK and Spalding RF, Effect of various materials in multilevel samplers on monitoring commonly occurring agrichemicals in ground water. *Ground Water Monit Remed* **16**:80–84 (1996).
7 Parker LV and Ranney TA, Sampling trace-level organic solutes with polymeric tubing. Part I. Dynamic studies. *Ground Water Monit Remed* **18**:148–155 (1998).
8 MacIntyre WG, Boggs M, Antworth CP and Stauffer TB, Degradation kinetics of aromatic organic solutes introduced

into a heterogeneous aquifer. *Water Resour Res* **29**:4045–4051 (1993).
9 Garabedian SP, LeBlanc DR, Gelhar LW and Celia MA, Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts. 2. Analysis of spatial moments for a non-reactive tracer. *Water Resour Res* **27**:911–924 (1991).
10 Barker JF, Patrick GC and Major D, Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monit Remed* **7**:64–71 (1987).
11 Widmer SK, Spalding RF and Skopp J, Nonlinear regression of breakthrough curves to obtain retardation factors in a natural gradient field study. *J Environ Qual* **24**:439–444 (1995).
12 Van Genuchten MTh and Alves WJ, Analytical solutions of the one-dimensional convective–dispersive solute transport equation, *USDA Tech Bull 1661*, USDA, Washington, DC, USA, (1982).
13 Roberts PV, Goltz MN and Mackay DM, A natural gradient experiment on solute transport in a sand aquifer. 3. Retardation estimates and mass balances for organic solutes. *Water Resour Res* **22**:2047–2058 (1986).
14 Bianchi-Mosquera GC and Mackay DM, An evaluation of the reproducibility of forced-gradient solute transport tests. *Ground Water* **32**:937–948 (1994).
15 Acton DW and Barker JF, *In situ* biodegradation potential of aromatic hydrocarbons in anaerobic groundwaters. *J Contam Hydrol* **9**:325–352 (1992).
16 Agertved J, Rügge K and Barker JF, Transformation of the herbicides MCPP and atrazine under natural aquifer conditions. *Ground Water* **30**:500–506 (1992).
17 Bianchi-Mosquera GC, *In situ* determination of transport parameters for organic contaminants in ground water, *Doctor of Environmental Science and Engineering Dissertation*, University of California, Los Angeles, USA, 189 pp (1993).
18 Widmer SK and Spalding RF, A natural gradient transport study of selected herbicides. *J Environ Qual* **24**:445–453 (1995).
19 Gillham RW, Starr RC and Miller DJ, A device for *in situ* determination of geochemical transport parameters. 2. Biochemical reactions. *Ground Water* **28**:858–862 (1990).
20 Nielsen PH, Bjarnadóttir H, Winter PL and Christensen TH, *In situ* and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume, 2. Fate of aromatic and chlorinated aliphatic compounds. *J Contam Hydrol* **20**:51–66 (1995).
21 Bjerg PL, Brun A, Nielsen PH and Christensen TH, Application of a model accounting for kinetic sorption and degradation to *in situ* microcosm observations on the fate of aromatic hydrocarbons in an aerobic aquifer. *Water Resour Res* **32**:1831–1841 (1996).
22 Nielsen PH, Bjerg PL, Nielsen P, Smith P and Christensen TH, *In situ* and laboratory-determined first-order rate constants of specific organic compounds in an aerobic aquifer. *Environ Sci Technol* **30**:31–37 (1996).
23 Bjerg PK, Rügge K, Cortsen J, Nielsen PH and Christensen TH, Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grindsted Landfill leachate plume: *in situ* microcosm and laboratory batch experiments. *Ground Water* **37**:113–121 (1999).
24 Nielsen PH, Albrechtsen H-J, Heron G and Christensen TH, *In situ* and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume, 1. Experimental conditions and fate of phenolic compounds. *J Contam Hydrol* **20**:27–50 (1995).
25 Papiernik SK and Spalding RF, Atrazine, deethylatrazine, and deisopropylatrazine persistence measured in groundwater *in situ* under low-oxygen conditions. *J Agric Food Chem* **46**:749–754 (1998).
26 Nielsen PH, Christensen TH, Albrechtsen H-J and Gillham RW, Performance of the *in situ* microcosm technique for measuring the degradation of organic chemicals in aquifers. *Ground Water Monit Remed* **16**:130–140 (1996).
27 Gillham RW, Robin MJL and Ptacek CJ, A device for *in situ* determination of geochemical transport parameters. 1. Retardation. *Ground Water* **28**:666–672 (1990).
28 Gamerdinger AP, Van Rees KCJ, Rao PSC and Jessup RE, Evaluation of *in situ* columns for characterizing organic contaminant sorption during transport. *Environ Sci Technol* **28**:376–382 (1994).
29 Ball WP and Roberts PV, Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium. *Environ Sci Technol* **25**:1223–1237 (1991).
30 van Genuchten MTh and Wagenet RJ, Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions. *Soil Sci Soc Am J* **53**:1303–1310 (1989).
31 Zipper C, Suter MJ-F, Haderlein SB, Gruhl M and Kohler H-PE, Changes in the enantiomeric ratio of (*R*)- to (*S*)-mecoprop indicate *in situ* biodegradation of this chiral herbicide in a polluted aquifer. *Environ Sci Technol* **32**:2070–2076 (1998).
32 Thurman EM, Barber LB Jr and LeBlanc D, Movement and fate of detergents in groundwater: a field study. *J Contam Hydrol* **1**:143–161 (1986).